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by Veronica M. Cepak and Charles R. Martin

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Preparation of Polymeric Micro- and Nanostructures Using A Template-Based Deposition Method

Veronica M. Cepak and C. R. Martin*

Department of Chemistry
Colorado State University
Fort Collins, CO 80523

* To whom correspondence should be addressed.

Email: crmartin@lamar.colostate.edu

ABSTRACT

Polymeric microtubules and nanofibrils have been prepared by depositing a solution of the desired polymer within the pores of microporous template membranes. Both microporous alumina and track-etched polyester membranes were used as the templates. Tubules and fibrils composed of polystyrene, poly(2,6-dimethyl-1,4-phenylene oxide), poly(vinylidene fluoride), poly(methyl methacrylate), poly(bisphenol A carbonate), and poly(lactic acid) have been prepared. Nanofibrils with diameters as small as 30 nm have been achieved. A concentric tubular composite microstructure consisting of an outer microtubule of polystyrene surrounding an inner microwire of polypyrrole has also been fabricated.

INTRODUCTION

We have been investigating a general method for preparing tubular and fibrillar micro- and nanostructures called template synthesis.¹⁻⁴ This method typically entails synthesizing the desired material within the pores of a microporous template membrane. The template membranes employed contain cylindrical pores, with monodisperse diameters, that extend through the entire thickness of the membrane. We have used both alumina and polymeric template membranes in our work. The template method has been used to prepare tubular and fibrillar micro- and nanostructures composed of metals, semiconductors, electronically conductive polymers, carbons, and other materials.¹⁻⁴

We have also shown that microtubules composed of the electronically insulating polymer polyacrylonitrile can be prepared by polymerization of acrylonitrile within the pores of the microporous alumina template membranes. These polyacrylonitrile tubules were subsequently pyrolyzed to yield the corresponding carbon tubules.^{5,6} Another research group has polymerized furfuryl alcohol within the pores of such alumina template membranes to prepare insulating polymeric tubules; these poly(furfuryl alcohol) tubules were also subsequently pyrolyzed to yield the corresponding carbon nanotubes.⁷

Template synthesis of polymeric fibrils has also been accomplished via the polymerization of methyl methacrylate within the pores of the alumina template membranes.⁸ Polyethylene fibrils have also been prepared by melting this polymer into the pores of such membranes.⁹ Finally, polymeric fibrils have

been synthesized in the channels of mesoporous silica using monomer vapor deposition followed by in situ polymerization.^{10,11}

We describe here a new template-based method for fabricating polymeric micro- and nanostructures. This method entails vacuum filtration of a solution of the desired polymer into the pores of the alumina and polyester template membranes. This method should be applicable to any polymer that can be dissolved in a solvent that is compatible with these template membranes. We also show that this method can be part of a multistep process to prepare concentric tubular microstructures in which an inner microwire of one material is surrounded by an outer microtubule composed of a second material.

EXPERIMENTAL

Materials. Polyester "track-etched" membranes with 1.0 μm , 400 nm and 30 nm-diameters pores were obtained from Poretics. Alumina membrane filters (Anodisc) with 200 nm-diameter pores were obtained from Whatman. The following polymers were used to prepare the fibrillar and tubular micro- and nanostructures described here: Polystyrene (M. W. 5000; Polysciences), poly(2,6-dimethyl-1,4-phenylene oxide) (M. W. 244,000; Aldrich), poly(vinylidene fluoride) (M. W. 534,000; Aldrich), poly(methyl methacrylate) (M. W. 12,000; Aldrich), poly(bisphenol A carbonate) (M. W. 32,000-36,000; Polysciences), and poly(lactic acid) (M. W. 50,000; Polysciences). ACS grade CH_2Cl_2 was used as the solvent for all polymer solutions. Materials used for the electrochemical deposition of polypyrrole were pyrrole (Sigma), methanol (ACS grade, Fisher),

NaCl (Mallinckrodt) and Milli-Q 18 MΩ H₂O. The pyrrole was distilled under N₂ prior to use.

Preparation of the Polymeric Tubules and Fibrils. These micro- and nanostructures were prepared by vacuum filtration of a 5 % (w/w) solution of the desired polymer into the pores of the template membrane. The polymer solution (~1 mL) was placed on the top side of the template membrane (1.2 cm² surface area) and vacuum (water aspirator) was applied to the bottom of the membrane. Vacuum was applied until the entire volume of the solution was pulled through the membrane, and the solvent evaporated. After the solvent had evaporated, the membrane was removed from the vacuum and then dissolved to free the tubules or fibrils that had been deposited within the pores. The polyester template membranes were dissolved in hexafluoroisopropanol (HFIP; Aldrich); 3 M NaOH (Mallinckrodt) was used to dissolve the alumina membranes. Polymeric tubules were obtained in the larger pore-diameter membranes (1.0 μm, 400 nm); solid nanofibrils were obtained in the smallest pore-diameter membranes.

Scanning Electron Microscopy (SEM). Microstructures prepared in the alumina membranes were imaged by first affixing the microstructure-containing membrane to an epoxy resin (Epoxy-Patch, Dexter Corp.). The surface of the membrane was then polished using fine grit sandpaper to remove any polymeric surface layer. This sample was then placed in 3 M NaOH to dissolve the alumina. This left an ensemble of the freed polymeric microstructures that

protruded from the epoxy surface like the bristles of a brush. The surface of this sample was sputtered with ~10 nm of Au prior to SEM imaging.

Micro- and nanostructures prepared in the polyester membranes were imaged by first affixing the microstructure-containing membrane to a piece of Cu-foil tape (3M Scotch No. 1739-7). The adhesive used in this tape does not dissolve in the solvent used to dissolve the template membrane, HFIP. The surface of the membrane was then gently wiped with a cotton applicator tip wetted with CH_2Cl_2 to remove any polymeric surface layer. This sample was then placed in HFIP to dissolve the polyester. The surface of this sample was then sputtered with Au and imaged.

Concentric Tubular Microstructures. Polyester template membranes (1 μm pore diameter, 20 μm thick) were used to prepare these composite microstructures. Polystyrene tubules were first deposited within the pores of these membranes using the method described above. The surface of this tubule-containing membrane was then wiped with CH_2Cl_2 to remove any polystyrene surface layer. A Au film was then sputtered onto one face of the membrane; this film was used as the working electrode for the electrodeposition of inner polypyrrole microwires within the outer polystyrene tubules. A piece of Cu tape was applied to one corner of the Au film to provide a working electrode contact.

The electrochemical cell consisted of a glass tube (1.2-cm diameter) with an o-ring joint on one end. The Au-coated membrane was clamped (Au side down) between the o-ring and a glass plate. The glass tube was then filled with

the electropolymerization solution, and a Ag/AgCl reference electrode (BAS RE-5) and a spiral Pt wire counter electrode (Alfa Aesar) were placed in this one-compartment cell.

Pyrrole was electropolymerized into the polystyrene microtubules at a constant anodic current of 0.5 mA cm^{-2} for 1 hour. The deposition solution consisted of 0.1 M pyrrole and 0.025 M NaCl in 1:2 (v/v) methanol/H₂O. Electrochemical depositions were carried out using a PAR Model 173 potentiostat. The pyrrole solution was purged with N₂ prior to and during electropolymerization. After deposition of the polypyrrole, a two-point conductivity measurement was obtained to show that the polypyrrole microwires extended through the complete thickness of the template membrane. This was accomplished by simply placing the probes of the multimeter on opposite sides of the membrane. Conductivity measurements were taken using a Keithly digital multimeter.

After electropolymerization of the polypyrrole microwires, both surfaces of the template membrane were polished with alumina powder to remove the Au film and any unwanted surface polymeric layers. The membrane was then attached to a piece of Cu tape and immersed in HFIP to remove the template membrane. SEM images were taken as described before. In addition, energy dispersive spectra (EDS) were obtained to identify the chemical composition of the composite microstructures prepared. A Kevex Super 8000 microanalysis system equipped with a Li drifted Si detector was used.

RESULTS AND DISCUSSION

The template-based polymer-deposition method described here is in some ways similar to Whitesides' capillary micromolding method.^{12,13} In this method, a low viscosity polymer precursor fills channels that are made when an elastomeric mold is placed in contact with a substrate. The channels are filled by capillary action. The mold can be removed, and the polymer precursor can be subsequently cross-linked to prepare patterned, free-standing polymer films.

In analogy to Whitesides' method, the pores of the alumina template membranes can also be considered as channels. However, vacuum is used to pull the solution through the channels (pores) in our template membranes. In addition, our method uses microporous membranes instead of micromolds as the templates, and we use polymer solutions instead of polymeric precursors to fill the pores. Finally, polymeric microstructures, instead of patterned films, are obtained from the method described here.

Polymeric Microtubules and Nanofibrils Prepared in the Polyester Template Membranes. Figure 1 shows SEM images of polystyrene tubules prepared in polyester templates with 1 μm -dia. pores. As discussed in the experimental section, the polyester membrane has been dissolved away to expose the polymeric tubules prepared in the pores. A 5% solution of the polymer was used to prepare the tubules in Figure 1A. As would be expected, these tubules have outside diameters that are equivalent to the pore diameter of the template membrane. Electron microscopy reveals no microscopic defects in these tubules. As a result, the lengths of these tubules are equivalent to the thickness

of the template membrane. This may be contrasted to tubules obtained from a 2.5% polymer solution (*vide infra*). Whether there contain defects that are beyond the resolution of the SEM is, at this, point undetermined.

Figure 1B shows polystyrene tubules that were prepared from a 2.5% polystyrene solution. These tubules contain defects in the tube walls, and tubules with lengths significantly smaller than the thickness of the template membrane are obtained. This suggests that these defective tubules do not have the mechanical integrity of the defect-free tubules shown in Figure 1A. The appearance of defects in the tubules obtained from the lower concentration solution may relate to the preference of the polystyrene to deposit on itself rather than on the pore wall. As a result of this tendency, at low concentrations there is insufficient polymer to completely coat the pore walls, and defective tubules are obtained.

Polystyrene nanofibrils were prepared in the 30 nm-pore-diameter polyester template membranes (Figure 1C). Only solid nanofibrils (as opposed to hollow microtubules) could be obtained in these very small pore-diameter membranes. Perhaps lower polymer concentrations might be used to prepare nanotubular structures in such membranes. We have not yet explored this issue. Figure 2 shows an SEM image of poly(phenylene oxide) tubules prepared within a polyester template with 400 nm-diameter pores. Again, the tubule outside diameter reflects the pore diameter of the template, and the tubule length is equivalent to the thickness of this template.

This tubule and fibril-preparation method should be applicable to any polymer that can be dissolved in a solvent that does not attack the template membrane. Since these membranes are extremely inert (to our knowledge, they dissolve only in HFIP), this method should be applicable to water-soluble polymers and polymers soluble in nearly all common organic solvents. However, if the template membrane is to be removed (as in Figures 1 and 2) it is clear that the microstructures prepared cannot be soluble in HFIP.

Polymer Microfibrils Prepared in the Alumina Template Membranes. Figure 3 shows SEM images of microfibrils composed of polystyrene, poly(vinylidene fluoride), poly(phenylene oxide), and poly(methyl methacrylate). Again, the alumina membrane has been dissolved to expose the polymeric fibrils prepared in the pores, and again, because of the small pore diameter solid fibrils instead of hollow tubules are obtained. Some residual polymeric surface layer is observed at the tops of these fibrils. Note the high density of fibrils; this reflects the very high porosity (>50%) of the alumina template membrane. The lengths of these fibrils show that they spanned the complete thickness (~50 μm) of the template membrane. As before, the fibril diameter is equivalent to the pore diameter (~200 nm) of the template.

This method should be applicable to any polymer that can be dissolved in a solvent that does not attack the alumina template. Since this template is soluble in aqueous solutions of HF and NaOH, this leaves almost any common organic solvent. Water-soluble polymers might be a problem with this membrane because the polymeric tubules would dissolve in the aqueous solutions used to

dissolve the template. This would not, however, be a problem in applications where the template did not have to be removed (e.g., the membrane applications described in reference 14).

Polystyrene/Polypyrrole Concentric-Tubular Composite Microstructures.

We have been interested in developing sequential tubule fabrication processes such that concentric tubular microstructures can be prepared.^{15,16} These composite microstructures consist of an outer tubule of one material that surrounds inner microtubules (or a microfibril) of other materials. Figure 4 shows that the tubule preparation method described here can be used as a step in the fabrication of such concentric tubular composites. In this case, an outer tubule of an insulating plastic (polystyrene) surrounds an inner microwire of an electronically conductive material (polypyrrole).

Figure 4A shows an SEM image of the polystyrene microtubules before deposition of the inner polypyrrole microwires. Figure 4B shows an analogous SEM after electrochemical deposition of the polypyrrole microwires. Note that the formerly empty (Figure 4A) microtubules are all now filled. After filling with the microwires, the membrane had a bluish-black color indicative of polypyrrole.

A two-point conductivity measurement was used to confirm that the inner filling was, indeed, polypyrrole. Prior to deposition of the polypyrrole, the polystyrene-containing template membrane had essentially infinite resistance across the membrane. After deposition of the polypyrrole microwires the transmembrane conductivity was on the order of 10^2 S cm^{-1} . This dramatic increase in conductivity shows that polypyrrole microwires that span the

complete thickness of the template membrane were deposited within the outer polystyrene tubules.

Energy dispersive spectroscopy (EDS) was also used to confirm the presence of the polypyrrole microwires. The polypyrrole microwires were deposited from a NaCl-containing solution and should, therefore, contain Cl⁻ as the counterion. Figure 5 shows an EDS spectrum for the concentric tubular composite after deposition of the polypyrrole. A strong Cl signal is seen. A Cl signal is not detected prior to polypyrrole deposition.

CONCLUSIONS

We have described a new template-based approach for preparing tubular and fibrillar micro- and nanostructures. This is a general method and should be applicable to any polymer that can be dissolved in a membrane-compatible solvent. Because of the very different chemistries of the two template membranes studied here (organic polymer vs. inorganic oxide), a membrane that is compatible with any desired solvent should be available. Hollow polymeric tubules were obtained in the large pore-diameter (1 μm) template membrane. Solid fibrillar nanostructures were obtained in the membranes with smaller pore diameters. Polystyrene tubules prepared in large pore-diameter polyester template membranes were used to fabricate polystyrene/polypyrrole composite microstructures. These composite microstructures can be viewed as polypyrrole microwires insulated by outer polystyrene microtubules.

This method is of interest because it adds to a growing tool box¹⁻⁴ of methodologies, useful with the template method, to prepare micro- and nanostructures. The most important aspect of this new method is that it can be used to prepare insulating polymers. As noted above, such polymeric tubules could serve as insulating coatings on template-synthesized electronically-conductive nanowires. Tubules composed of ionically conductive polymers might also serve as separators in template-synthesized concentric-tubular microbatteries.

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FIGURE CAPTIONS

Figure 1 Scanning electron micrograph of (A) defect-free 1 μm -outside-diameter polystyrene microtubules prepared from a 5 % (w/w) polymer solution in CH_2Cl_2 . (B) As per A but prepared from a 2.5 % (w/w) polymer solution in CH_2Cl_2 . Note broken and defective tubules. C. Polystyrene nanotubules prepared in the 30 nm pore-diameter polyester template membrane. Solution as per A.

Figure 2 Scanning electron micrograph of poly(phenylene oxide) microtubules prepared in the 400-nm pore-diameter polyester membrane.

Figure 3 Scanning electron micrographs of microfibrils prepared in the alumina template membrane. (A) polystyrene. (B) poly(vinylidene fluoride). (C) poly(phenylene oxide). (D) poly(methyl methacrylate).

Figure 4 Scanning electron micrographs of (A) polystyrene microtubules prepared in the 1 μm pore-diameter polyester template membrane. (B) As per A but after electropolymerization of the inner polypyrrole microwires.

Figure 5 Energy dispersive spectra of the polystyrene/polypyrrole composite microstructures. A Cl emission peak is observed in the spectra which is

indicative of the Cl⁻ dopant in the electropolymerized polypyrrole. The EDS also showed emissions characteristic of Au and Pd. These impurities were introduced by sputtering the sample prior to SEM imaging.

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